

3.1 Crystal Binding.

Four basic types of binding, connected mainly with the chemical properties of the materials:

- van der Waals: weak, low T only
- ionic: strong between electroneg + pos elements
- metallic: most common for elements + alloys
- covalent: specific chemical bonds; CO₂ etc.

Definition. Cohesive energy = energy added to each formula unit to break a solid apart into neutral free atoms. (ions. → 'Lattice energy')
per formula unit.

Measured in eV. Wide range across periodic table: C = 7.4 eV W = 8.9 eV Ne = 0.02 eV

Strong correlation with melting point, especially among metals. W = 3700 K highest.

3.2 Inert gas crystals.

Closed shells: Ne $2s^2 2p^6$ Ar $3s^2 3p^6$ Kr Xe etc.

Ionization energy is very high, so ions would discharge in forming a crystal / solid.

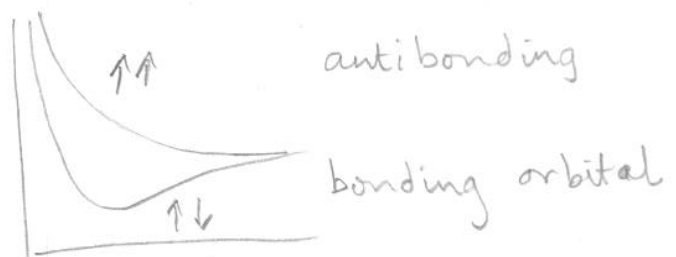
Closed shell remains in crystal. Force atoms together:

- ↳ core repulsion (Pauli)
- weak van der Waals attraction

London interaction
"induced dipole-dipole" interaction

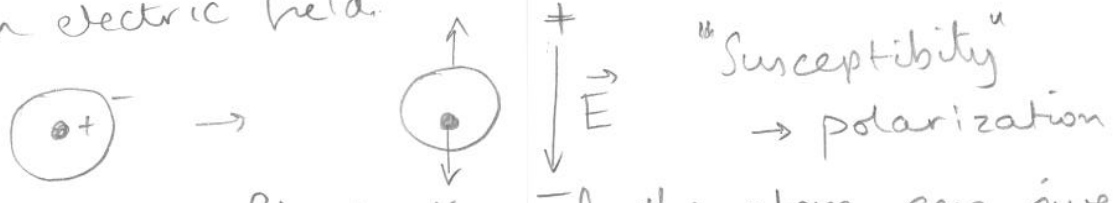
Pauli principle: two electrons with the same spin do not want to share the same space, so repel by an amount \propto overlap of wavefunctions

[opposite spin → attraction, see later]
Closed shells have all electrons paired, $\uparrow\downarrow$, so no possibility of bonding.

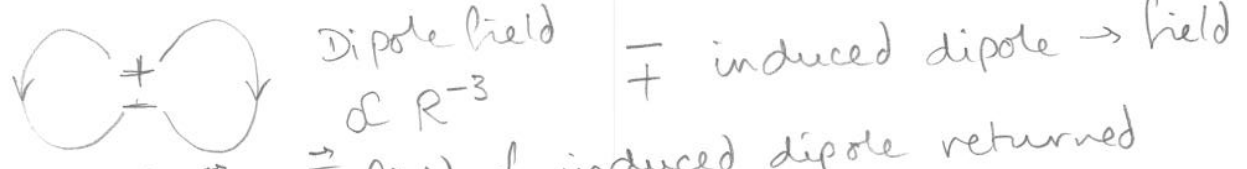


Dipole-dipole interaction.

Electron cloud can be displaced relative to nucleus by an electric field.



A spontaneous fluctuation of the atom can give a momentary displacement dipole, $p = ed$.



Energy of $\vec{p} \cdot \vec{E}$ -field of induced dipole returned to the original dipole = $(R^{-3})(R^{-3})$.

Energy is lowered \Rightarrow attractive interaction of R^{-6}

Fluctuation is driven by zero-point energy of th

3.3 Lennard-Jones potential "6-12"

$$U(R) = 4\epsilon \left[\left(\frac{\sigma}{R}\right)^{12} - \left(\frac{\sigma}{R}\right)^6 \right] = \frac{A}{R^{12}} - \frac{B}{R^6}$$

i) the R^{-12} is completely ad-hoc. We will see later that the choice of this function makes little difference to the results. Could be $\exp(-R/\rho)$

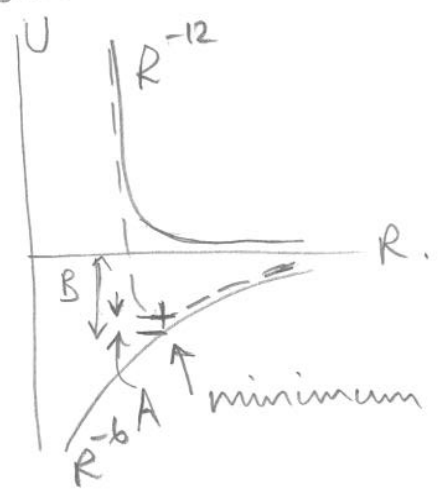
ii) two competing interactions needs 2 independent

23.01.06 I scale factors, choose $A = 4\epsilon\sigma^{12}$ $B = 4\epsilon\sigma^6$ without loss of generality.

σ is then a distance similar in size to R which is convenient if we switch units.

iii) 1st term repulsive, steep
2nd term attractive, gentle

Can see at minimum that $|B| \gg |A|$. typ. few % so form of A unimportant



SECTION B

7. State the assumptions that lie behind Bragg's law, $2d \sin \theta = \lambda$ that relates the angle of incidence, θ , of an X-ray beam of wavelength λ onto planes of a crystal spaced distance d apart which gives rise to a strong diffraction peak. We will now consider the reciprocal space view of Bragg's law.

[2]

Draw a detailed diagram showing the positions of the atoms in a crystal of Nickel which is known to have the face-centred cubic (fcc) structure with lattice parameter, a_0 . Label the axes along the edges of the conventional cubic unit cell and list the coordinates of all the atoms within the cell. Explain how the structure is decomposed into a lattice and a basis, following the cubic convention.

[5]

What is the reciprocal lattice of this cubic lattice? Draw a sketch of the reciprocal lattice and label the points according to their Miller indices. Which lattice points correspond to allowed reflections and which are disallowed by the fcc structure? What is the length of the general (hkl) reciprocal lattice vector. Show, with the aid of a sketch, which lattice planes in the crystal correspond to the (111) reciprocal lattice point.

[9]

Draw a vector diagram showing how to construct the directions of the incident and exit X-ray beams that correspond to diffraction from the (hkl) reciprocal lattice point. Hence derive an expression for the length of the reciprocal lattice vector and the angle between these two beams, which we will call γ . In an experiment using X-rays of wavevector $k = 40.8 \text{ nm}^{-1}$, a powdered Nickel sample is found to produce its first three diffraction peaks at angles, $\gamma = 45.4^\circ, 52.8^\circ$ and 78.0° . What are the corresponding lengths of the reciprocal lattice vectors? Demonstrate that these are consistent with an fcc structure and deduce the lattice constant, a_0 .

[8]

8. Justify the use of the Lennard-Jones (LJ) potential function to model the interaction potential between two atoms of inert gas separated by a distance, R ,

$$U(R) = 4\epsilon \left[\left(\frac{\sigma}{R} \right)^{12} - \left(\frac{\sigma}{R} \right)^6 \right].$$

What is the meaning assigned to the parameters σ and ϵ ?

[6]

All the inert gases (except Helium) crystallise in the face-centred cubic (fcc) structure. Write down an expression for the cohesive energy of an inert gas solid using the LJ potential. At low temperatures, you can consider this to be purely potential energy. You may use the numerical evaluations of the lattice sums, $P_6 = 14.45392$ and $P_{12} = 12.13188$, which are defined as $P_n = \sum_j p_j^{-n}$, where p_j is the distance of the j 'th site from the origin of the fcc lattice in units of the nearest-neighbour distance, summed over the entire lattice.

[10]

3.4 FCC LJ solid.

$U(R)$ applies to every pair of atoms in the solid. We neglect Kinetic Energy contributions as they only matter at high temperatures. LJ is always attractive, so close-packing favoured.

FCC = HCP for 1st neighbours (12)
FCC > HCP for higher-order shells

For crystal of N atoms, all identical

$$U_{tot} = \frac{1}{2} N (4\epsilon) \left[\sum_j \left(\frac{\sigma}{p_j R} \right)^{12} - \sum_j \left(\frac{\sigma}{p_j R} \right)^6 \right]$$

where p_j is a dimensionless geometry factor for the j 'th neighbour in the crystal. $R \rightarrow R_{n,n}$ [$p_1=1$]

The \sum 's are properties of the lattice only:

	FCC	HCP.	
$\sum p_j^{-12}$	12.1319	12.1323	≈ 12 neighbours
$\sum p_j^{-6}$	14.4539	14.4549	

Small differences favour FCC structure.

Find R : lowest energy distance in solid

$$\frac{dU_{tot}}{dR} = 2N\epsilon \left[-12(12.13) \frac{\sigma^{12}}{R^{13}} + 6(14.45) \frac{\sigma^6}{R^7} \right] = 0$$

$$\text{Gives } R_0 = 1.09 \sigma = \left(\frac{12 \times 12.13}{6 \times 14.45} \right)^{1/6} \sigma.$$

σ measured from gas phase properties

$$R_0/\sigma = 1.14 (\text{Ne}) \quad 1.11 (\text{Ar}) \quad 1.10 (\text{Kr}) \quad 1.09 (\text{Xe})$$

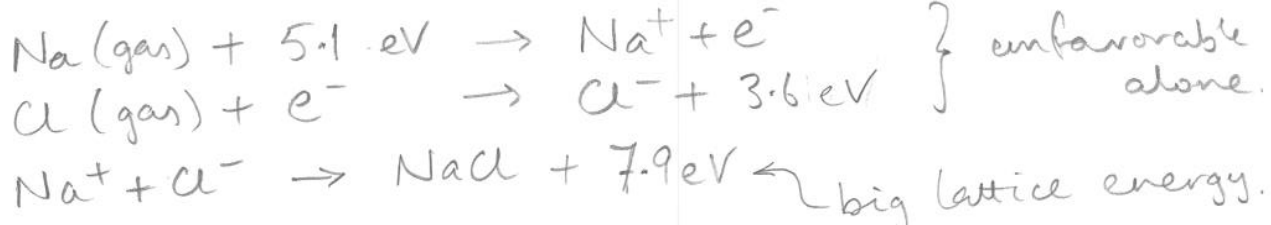
$U_{tot} = -2.15 (4N\epsilon)$ also agrees well.

~ 0.02 to 0.16 eV

$$2 \times 2.15 = -\cancel{12.13} \times (1.09)^{-12} + 14.45 \times (1.09)^{-6} \\ 4.30 \quad - 8.61$$

3.5 Ionic Crystals

Especially favoured for nearly closed-shell atoms which favour losing/gaining electrons → closed shell.



Cohesive energy = 7.9 + 3.6 - 5.1 = 6.4 eV

26.01.09 II

- For charged ions, the Van der Waals force is completely swamped by the Coulomb force.
- More complicated because of alternating signs.

Proceed as before, this time with exponential repulsion term, only for nearest neighbours. [even less important because of R⁻¹ Coulomb]

$$U_j = \begin{cases} \lambda \exp(-R/p) - \frac{q^2}{4\pi\epsilon_0 R} & \text{nearest n's.} \\ \pm \frac{q^2}{4\pi\epsilon_0 (p_j R)} & \text{all other neighbours.} \end{cases}$$

U_{tot} = N (zλ e^{-R/p} - $\frac{\alpha q^2}{4\pi\epsilon_0 R}$) after summing.

Z = number of nearest neighbours.

α = ∑_j (±) / P_j = Madelung constant. (later)

dU_{tot}/dR = - Nzλ / p e^{-R/p} + Nαq² / 4πϵ₀R² = 0 at R = R₀

⇒ R₀² exp(-R₀/p) = pαq² / 4πϵ₀zλ gives R₀

and U_{tot} = - $\frac{N\alpha q^2}{4\pi\epsilon_0 R_0} \left(1 - \frac{p}{R_0} \right)$

Madelung energy → Coulomb → repulsive part < 10%.

(25a)

$$U_{\text{tot}} = N \left(z\lambda e^{-R/p} - \frac{\alpha q^2}{4\pi\epsilon_0 R} \right)$$

$$\frac{\partial U_{\text{tot}}}{\partial R} = Nz\lambda \frac{-1}{p} e^{-R/p} + \frac{N\alpha q^2}{4\pi\epsilon_0} \frac{1}{R^2} = 0$$

$$\text{at } R=R_0, \quad Nz\lambda e^{-R_0/p} = \frac{N\alpha q^2}{4\pi\epsilon_0} \frac{p}{R_0^2}$$

$$\begin{aligned} \Rightarrow U_{\text{min}} &= \frac{N\alpha q^2}{4\pi\epsilon_0} \left(\frac{p}{R_0^2} - \frac{1}{R_0} \right) \\ &= -\frac{N\alpha q^2}{4\pi\epsilon_0 R_0} \left(1 - \frac{p}{R_0} \right) \end{aligned}$$

3.6 Madelung sum

Famous classical physics problem, stated by Madelung, solved by Ewald.

1D case is fairly easy:



$$\alpha = \sum_j \frac{(\pm)}{P_j}$$

j'th neighbour $R_j = jR = P_j R$, so $P_j = j$
alternating signs and counting both directions

$$\alpha = 2 \left[\frac{1}{1} - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} \dots \right] = 2 \ln 2 = 1.386.$$

look up series or use known functions

$$\ln(1+x) = x - \frac{x^2}{2} + \frac{x^3}{3} - \frac{x^4}{4} \dots \text{ weakly convergent}$$

3D case is very hard because number of distant neighbours mounts up very rapidly. Ewald method is to group the terms into charge-neutral shells:

$\alpha(\text{NaCl}) = 1.748$
 $\alpha(\text{CsCl}) = 1.763$
 $\alpha(\text{ZnSe}) = 1.638$ } "conditionally convergent"
→ NaCl offset by more neighbours. (Pauli)

25.01.10.
23.01.06 II

3.7 Atomic/Ionic Radii

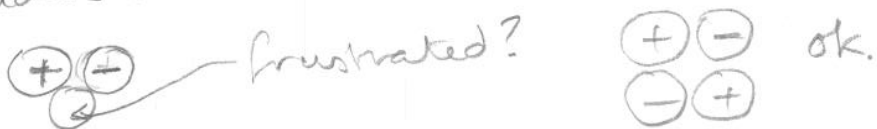
We have seen sphere-packing to be an important factor in choice of structure. When atoms all have the same size, this works. But 2 or more sizes means that other structures become possible.

Uncharged spheres: hcp & fcc, hex planes

Charged +/- ions: square arrays > hexag.

- still little distinction NaCl / CsCl

ionic radius: next level of detail.



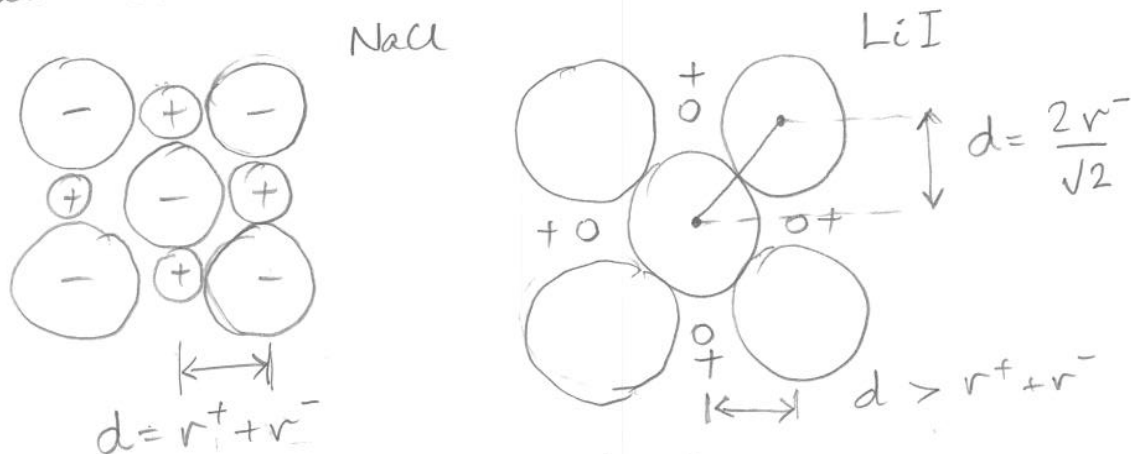
Alkali halides:

All monovalent ions (Li Na K Rb Cs) (F Cl Br I)

If we measure the electron density with detailed X-ray diffraction, we see very spherical shape [pic].

- All have NaCl structure, except Cs (Cl, Br, I)
- Look at table of ion spacings, d as measured.
- Model as sum of 2 radii. works within few % except for bottom left corner where errors get up to 8%. [pic].

Reason is that the big anions (-ve) start to touch each other.



Crossover when $r^+ + r^- = \sqrt{2} r^-$
 $r^+ = r^- (\sqrt{2} - 1)$

$$\frac{r^-}{r^+} = (\sqrt{2} - 1)^{-1} = 2.414$$

This crossover was originally used by Pauling to determine the relative sizes of the anions and cations.

Method works well for oxides also, except that a correction is needed for the coordination number (of neighbours): more neighbours means larger radius.

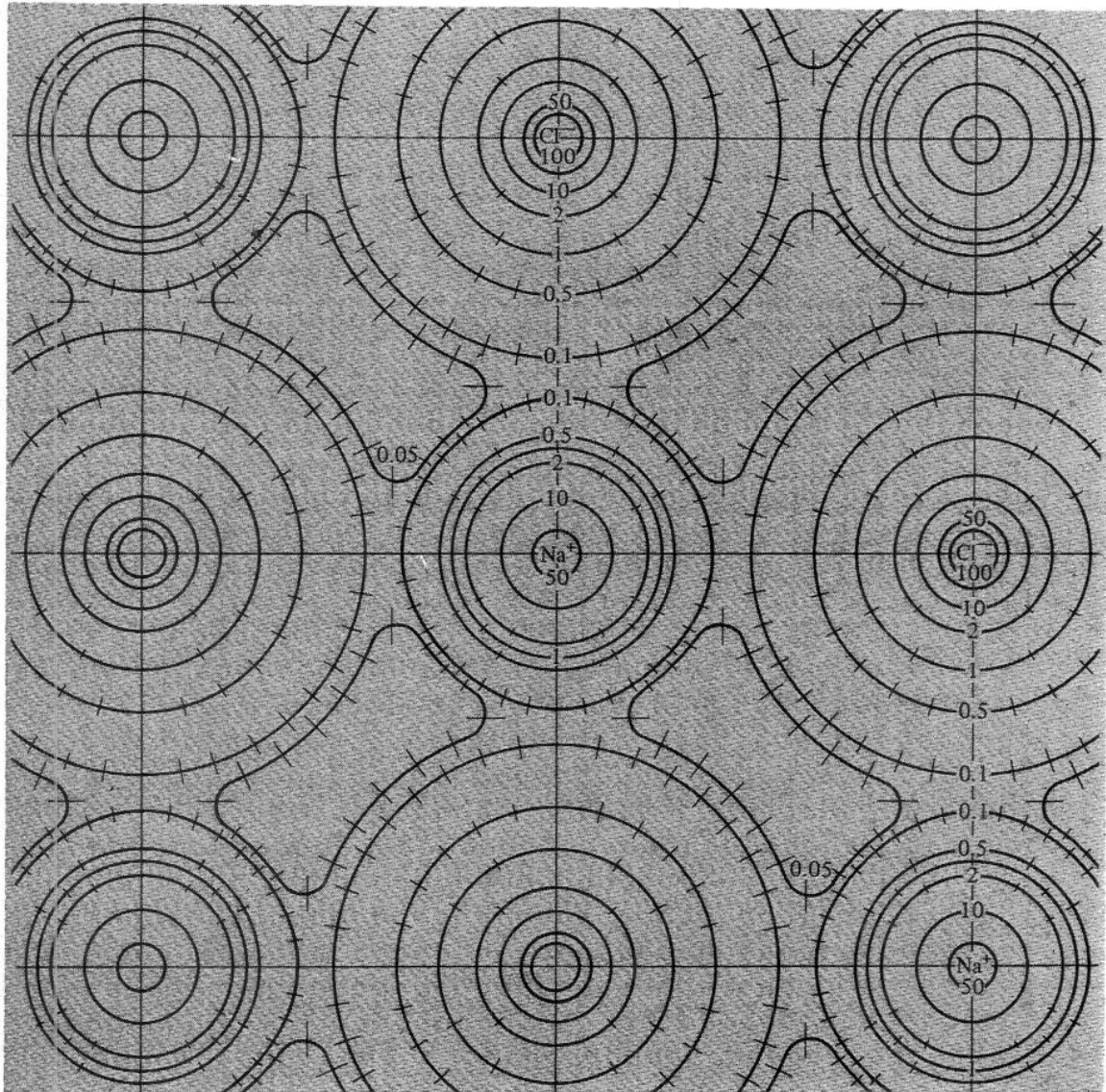


Figure 19.5

Electronic charge density in a $[100]$ plane of NaCl containing the ions, as inferred from X-ray diffraction data. The numbers give the values of the density along lines of constant density, in units of electrons per cubic angstrom. The lines perpendicular to the constant density curves are error bars. (After G. Schoknecht, *Z. Naturforschung* **12**, 983 (1957).)

Table 9 Atomic and ionic radii

Values approximate only. Units are $1 \text{ \AA} = 10^{-10} \text{ m}$. For original references see W. B. Pearson, *Crystal chemistry and physics of metals and alloys*, Wiley, 1972.

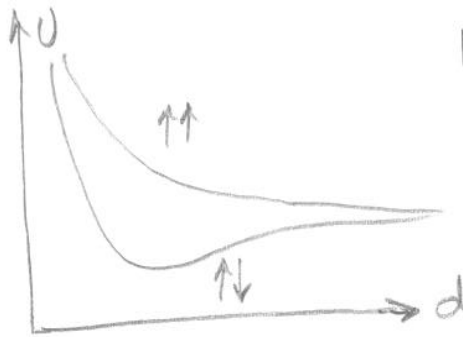
H	2.08																	He																				
Li	0.68	Be	0.35																	Ne	1.58																	
	1.56		1.06																		0.64																	
			1.13																																			
Na	0.97	Mg	0.65																	Ar	1.88																	
	1.91		1.40																		0.99																	
			1.60																																			
K	1.33	Ca	0.99	Sc	0.81	Ti	0.68	V		Cr		Mn		Fe		Co		Ni		Cu		Zn		Ga		Ge		As		Se		Br		Kr		2.00		
	2.38		1.98		1.64		1.46		1.35		1.28		1.26		1.27		1.25		1.25		1.28		1.39			1.41		1.37		1.39								
Rb	1.48	Sr	1.13	Y	0.93	Zr	0.80	Nb	0.67	Mo		Tc		Ru		Rh		Pd		Ag		Cd		In		Sn		Sb		Te		I		Xe		2.17		
	2.55		2.15		1.80		1.60		1.47		1.40		1.36		1.34		1.35		1.38		1.45		1.57			1.66		1.55		1.59								
Cs	1.67	Ba	1.35	La	1.15	Hf	1.58	Ta		W		Re		Os		Ir		Pt		Au		Hg		Tl		Pb		Bi		Po		At		Rn				
	2.73		2.24		1.88		1.58		1.47		1.41		1.38		1.35		1.36		1.39		1.44		1.57			1.72		1.75		1.76								
Fr	1.75	Ra	1.37	Ac	1.11																																	

Ce	1.01	Pr		Nd		Pm		Sm		Eu		Gd		Tb		Dy		Ho		Er		Tm		Yb		Lu	
	1.71		1.83		1.82		1.81		1.80		1.80		1.80		1.78		1.77		1.77		1.76		1.75		1.74		1.94
	1.82																										
Th	0.99	Pa	0.90	U	0.83	Np		Pu		Am		Cm		Bk		Cf		Es		Fm		Md		No		Lr	
	1.80		1.63		1.56		1.56		1.58		1.64		1.81														

← Standard radii for ions in inert gas (filled shell) configuration →
 ← Radii of atoms when in tetrahedral covalent bonds →
 ← Radii of ions in 12-coordinated metals →

3.8 Covalent Crystals

Pauli principle for unfilled shells allows bonds



No exclusion for ↑↓

When electron is nearer 2 nuclei it can reach a lower energy than just one.

Chemical properties take over: "bonds"

i) Fixed directions determined by hybridization:

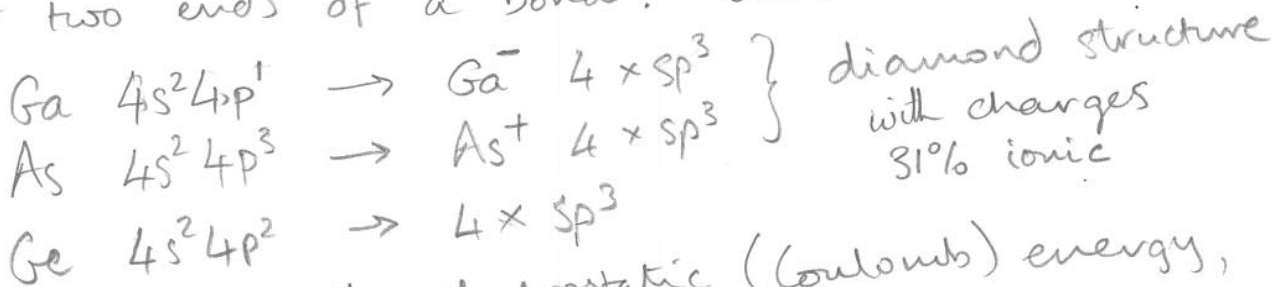
- 4 electrons : $s^2p^2 \rightarrow 4 \times sp^3$ tetrahedral
- [5 electrons : $s^2p^3 \rightarrow 3 \times p$ orthorhombic]
- 3 electrons : $s^2p \rightarrow 3 \times sp^2$ hexagonal.

ii) Bond lengths strongly constrained

- gives open lattice-like structure. 0.34 vs 0.74
- density of packing relatively unimportant.

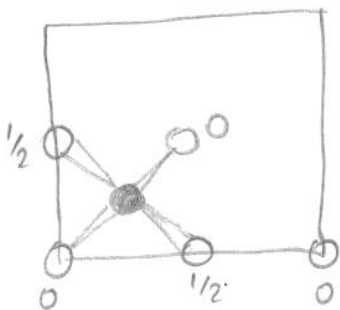
Ball-and-stick models appropriate here.

Crossover between covalent and ionic structure is often discussed. Partial charges can appear at two ends of a bond: GaAs



To minimise the electrostatic (Coulomb) energy, GaAs sites are rigidly defined in lattice

- no Ga-Ga or As-As bonds.



Diamond structure
 \rightarrow Zinc Blende (ZnS) structure
 Bond angles all $109^\circ = \cos^{-1}(-1/3)$

3.9 Metals

Yet another configuration: ions + "free" electrons.

Electrons keep apart by Pauli repulsion
(we will see how later on.)

Electrons determine most of the properties:

- compress too much \rightarrow increase overlap energy
- separate too much \rightarrow electrons must return to ions, losing benefit of spreading/sharing.

Electrons largely screen ions from each other.

Structure determined by maximum separation of ions (screened Coulomb repulsion).

\rightarrow close packed hcp & fcc structures.

Cases where less dense structures form

eg W, Mo, Ta are bcc, it is the shape of the d-orbitals that interferes with the close-packing.

Filled d-orbitals are also important for the high-group transition metals, where the ionic radius \approx metallic radius

Ag 1.26 / 1.45 Au 1.37 / 1.44 Cd 0.97 / 1.57

- (c) Show that the density of states per unit length is given by

$$g(E) = \frac{1}{\pi a V \sqrt{1 - \left(\frac{E}{2V}\right)^2}}$$

You may find the following facts useful: the number of states per unit length with values of k in the range $k \rightarrow k + dk$ is given by $g(k)dk = dk/2\pi$; electrons have two spin states; $\varepsilon(k) = \varepsilon(-k)$.

[8]

- (d) Since $\varepsilon(k) = \varepsilon(-k)$ we can define the Fermi wave vector k_F by $E_F = \varepsilon(k_F)$, with $k_F > 0$. The number of electrons per atom is given by $N = a \int_{-\infty}^{E_F} g(E)dE$. Rewrite this equation in terms of $g(k)$ and k_F , and find N as a function of k_F .

[3]

For hydrogen $E_F = 0$. Find the corresponding value of k_F , and hence the number of electrons per atom.

[3]

8. This question is about bonding in silicon.

- (a) Draw a plot of the variation of the interaction energy (ϕ) of a pair of neutral atoms as a function of their separation r . On this graph indicate the distance r_0 and energy $-\epsilon$ at which the system is in equilibrium.

[4]

- (b) What is the main physical mechanism leading to the form of the interaction energy at short distances?

[2]

Silicon likes to form bonds with exactly four neighbouring atoms. What kind of bonding holds the atoms together? Give reasons.

[2]

- (c) Silicon exists in the diamond structure in which each atom has four neighbours. For silicon we can write the interaction energy between neighbours as

$$\phi(r) = \phi_0 \{ \exp(-2\alpha(r-d)) - 2 \exp(-\alpha(r-d)) \}$$

Write the energy per atom (U) when the bond length is r in terms of $\phi(r)$?

[1]

Now find the equilibrium bond length r_0 and energy U_0 .

[4]

- (d) The volume per atom (V) in the diamond structure is $(8/\sqrt{27})r^3$. The bulk modulus is given by

$$B = V \frac{\partial^2 U}{\partial V^2}$$

Show that the bulk modulus of silicon is $B = \alpha^2 \phi_0 / (2\sqrt{3}r_0)$.

[4]

- (e) The model for the energy that we have been using assumes that the energy depends only on the length of the bonds between atoms. Suggest another quantity on which the energy depends strongly, and give an example of a distortion of the lattice for which it is important.

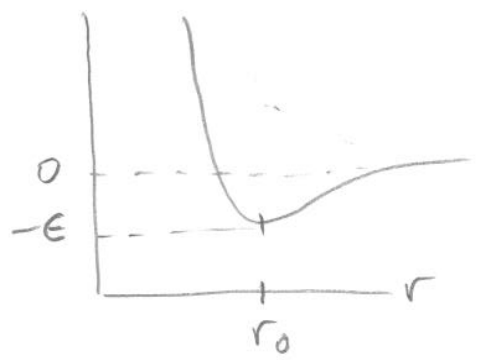
[3]

9. This question is about a free electron model of the thermal properties of aluminium.

- (a) A free electron metal is characterised by two energies: the Fermi energy and the work function. The state the connection between the two.

[2]

Exam 2005 Q8.



- Attractive + Repulsive terms.
- Covalent: unfilled shell.

(c) Ignore: 2nd neighbours.
Thermal motion (kinetic energy)

$$U = \sum_{\text{n.n.'s}} \phi(r_j) = \sum_{\text{n.n.'s}} \phi(r) \quad \text{since all n.n.'s have } r_j = r.$$

N atoms in sample, use N/2 to avoid double counting

$$U = \frac{N}{2} 4 \phi(r) = 2N \phi(r)$$

$$\frac{dU}{dr} = 2N \phi_0 \left\{ \begin{array}{l} -2\alpha e^{-2\alpha(r-d)} \\ + 2\alpha e^{-\alpha(r-d)} \end{array} \right\} = 0 \quad \text{at } r=r_0$$

$$\Rightarrow 2\alpha(r_0 - d) = \alpha(r_0 - d) \Rightarrow r_0 = d$$

$$U_0 = 2N \phi_0 \{ 1 - 2 \} = -2N \phi_0$$

(d) $B = V \frac{\partial^2 U}{\partial V^2} = V \frac{\partial}{\partial V} \left(\frac{\partial r}{\partial V} \frac{\partial U}{\partial r} \right) = V \frac{\partial r}{\partial V} \frac{\partial}{\partial r} \left(\frac{\partial r}{\partial V} \frac{\partial U}{\partial r} \right)$

$$\frac{\partial r}{\partial V} = \left(\frac{\partial V}{\partial r} \right)^{-1} = \left(\frac{8}{\sqrt{27}} 3r^2 \right)^{-1}$$

$$B = V \frac{\partial r}{\partial V} \frac{\partial}{\partial r} \left(\frac{\sqrt{27}}{8} \frac{1}{3r^2} 2N \phi_0 2\alpha \left\{ \begin{array}{l} -2\alpha(r-r_0) \\ -e^{-2\alpha(r-r_0)} \\ + e^{-\alpha(r-r_0)} \end{array} \right\} \right)$$

$$= \frac{8}{\sqrt{27}} r^3 \frac{\sqrt{27}}{8} \frac{1}{3r^2} \frac{\sqrt{27}}{2} \frac{N \phi_0 \alpha}{3} \left\{ \begin{array}{l} -2 \left(\frac{-2\alpha(r-r_0)}{r^3} (-e^{-2\alpha(r-r_0)}) + \frac{\alpha(r-r_0)}{r^3} e^{-\alpha(r-r_0)} \right) \\ + \frac{1}{r^2} \left(2\alpha e^{-2\alpha(r-r_0)} - \alpha e^{-\alpha(r-r_0)} \right) \end{array} \right\}$$

evaluate at $r=r_0$

$$B = \frac{1}{2\sqrt{3} r_0} N \phi_0 \alpha^2 \quad \text{for } N \text{ atoms, } \div N \text{ per atom}$$

(e) Bond angles, sensitive to shear distortion

